Energy, Mines and Resources Canada | Énergie, Mines et Ressources Canada

CANMET

Canada Centre for Mineral and Energy Technology | Centre canadien de la technologie des minéraux et de l'énergie

CEMENTATION OF SILVER AND COPPER ON LEAD DUST AND CHEMICAL UPGRADING OF THE CEMENT PRODUCT

D.J. MacKinnon, J.E. Dutrizac and D.J. Hardy
Metallurgical Chemistry Section
Extractive Metallurgy Laboratory

March 1985

Project: MRP-3.4.0.2.02
Hydrometallurgical Lead Process

This document is [illegible] (CANMET)

[illegible] rédigé [illegible] de [illegible] (CANMET)

19 MP

MINERALS RESEARCH PROGRAM
MINERAL SCIENCES LABORATORIES
DIVISION REPORT MRP/MSL 85-46 (TR)

MICROMEDIA

CEMENTATION OF SILVER AND COPPER ON LEAD DUST AND CHEMICAL UPGRADING OF THE CEMENT PRODUCT

by

D.J. MacKinnon*, J.E. Dutrizac* and D.J. Hardy**

ABSTRACT

Recovery of silver and copper from simulated spent iron chloride leaching solutions containing 1,500 mg/L Cu and 30 mg/L Ag was achieved by cementation on lead dust at 85°C. The preferred cementation procedure involves the single stage addition of 2X stoichiometric lead dust for 15 min under an N_2 atmosphere to yield a solution containing <1 mg/L of either Ag or Cu. The cement product contains ∿50% Pb, ∿40% Cu, ∿1% Ag and significant amounts of chloride. Leaching of the cement product with either 4-8 M HCl or sub-stoichiometric amounts of $FeCl_3$ (relative to lead) yields an upgraded cement product containing <10% Pb, ∿80% Cu and ∿2% Ag; such feeds are likely acceptable to many copper smelters although residual chloride contents may be a concern.

---

* Research Scientist and ** Research Technologist, Mineral Sciences Laboratories, CANMET, Energy, Mines and Resources Canada, 555 Booth Street, Ottawa, Ontario K1A 0G1.

INTRODUCTION

CANMET is currently investigating hydrometallurgical lead processing techniques as an alternative to lead smelting. Although the aqueous route is not without its own problems, it offers a number of advantages or potential advantages over conventional pyrometallurgical methods (1,2). Elemental sulphur is the dominant sulphidic leaching product, thereby avoiding the difficulties associated with the collection and treatment of dilute SO_2 gas streams from conventional sinter strand-blast furnace units. The aqueous approach can likely meet any reasonable ambient air requirements for lead whereas it is not at all clear that smelting practice, even modern practice, can achieve such ends. A pure lead product can be electrowon from the $PbCl_2$, thereby avoiding the health and materials handling problems associated with conventional lead fire refining. All of the new smelting processes will require an additional lead refining step. Lastly, the aqueous route offers potential economic advantages, especially for small-scale operations such as might result from lead production at individual mine sites.

The CANMET hydrometallurgical lead process utilizes prolonged ferric chloride leaching of lead concentrates at $\sim 100^{\circ}C$ to extract lead and silver values, followed by liquid/solids separation and lead chloride crystallization. The $PbCl_2$ crystals are then electrowon in either an aqueous or fused salt cell, and the solution is purified/regenerated prior to recycle to the leaching stage. Figure 1 illustrates a schematic flowsheet of the hydrometallurgical lead process utilizing the fused salt electrolysis option. Furthermore, a somewhat similar flowsheet has been devised to treat pyritic Zn-Pb-Cu-Ag bulk concentrates and that flowsheet also produces $PbCl_2$ crystals for electrolysis. For either flowsheet, the solution

exiting the leaching stage contains small amounts of dissolved silver and copper. These metals must be eliminated from the solution both to recover their values and to prevent their contaminating the $PbCl_2$ crystals subsequently formed by cooling the solution. A high purity lead chloride product is especially important for the fused salt recovery of lead as the dried crystals are fed directly into the fused salt cell without any further purification.

In the CANMET process, it is proposed to remove both silver and copper from the hot, clarified solution using cementation on lead dust. This report describes some preliminary bench scale tests designed to study both the cementation step as well as the subsequent chemical upgrading of the cement product. The primary objective of the cementation step was to produce a solution containing <1 mg/L of either Ag or Cu; the secondary objective was to yield a cement product as rich in Ag and Cu as possible. The goal of the chemical upgrading work was to yield a Ag-Cu product low enough in lead to be attractive to a copper smelter, and to achieve high recoveries of both metals.

EXPERIMENTAL

CEMENTATION

All test work was done using simulated spent leaching solutions containing 50 g/L Fe^{2+} (as $FeCl_2$), 40 g/L Zn^{2+} (as $ZnCl_2$), 3 M NaCl and 0.3 M HCl. Granular lead was initially added to 1 L of the test solution to reduce all iron to the ferrous state; the granular lead was present during the heat-up period (to $\sim 70^{\circ}C$), but was discarded prior to the addition of Ag and Cu and the start of the tests. After removal of the granular lead, the solution was heated under a N_2 atmosphere to the $85^{\circ}C$ test temperature

which earlier work had shown to be optimum for the reaction (3). Processing considerations suggested that the clarified pregnant leach solution (Fig. 1) would contain ∿1,500 mg/L Cu and ∿30 mg/L Ag; accordingly, just prior to the start of an experiment, 1500 mg/L Cu (as solid CuCl) and 30 mg/L Ag (10 mL of 3 g/L Ag as $AgNO_3$ stock reagent) were added to the solution and a sample was taken for analysis. Fine lead dust was then added to the solution which was agitated at 800 rpm; the amount of lead dust was calculated as a fraction of the stoichiometric requirement based on the initial Cu^+ and Ag^+ concentrations.

$$Pb + 2Cu^+ \longrightarrow Pb^{2+} + 2Cu \qquad (1)$$

$$Pb + 2Ag^+ \longrightarrow Pb^{2+} + 2Ag \qquad (2)$$

The test parameters studied included the stoichiometric amount of lead added, the retention time, and the method of lead addition.

At the end of the desired cementation time, the slurry was filtered hot, and the residue was rinsed with water and dried. The dried residue was then slurried in near-boiling water for ∿15 min to try to dissolve any residual NaCl or other chlorides. The slurry was filtered hot and the residue was dried. A portion of this dried residue was carefully weighed and dissolved in aqua regia. The solution was diluted to a known volume and was analyzed for Ag, Cu and Pb by atomic absorption spectrophotometry (AA) to yield the residue composition. The Ag and Cu concentrations in the initial and final solutions subjected to cementation were also determined by AA analysis.

CHEMICAL UPGRADING

Based on the optimum conditions identified in the cementation tests, cement products were prepared by reacting a 2X stoichiometric amount of lead dust with 1 L of solution containing 50 g/L Fe^{2+} as $FeCl_2$, 40 g/L Zn^{2+} as $ZnCl_2$, 3 M NaCl and 0.3 M HCl to which was added 1500 mg/L Cu as CuCl and 30 mg/L Ag as a $AgNO_3$ stock solution. The reaction was carried out at 85°C for 30 min and with vigorous agitation. The cement product was filtered hot, treated with boiling water to remove residual chlorides and then air dried. The various batches of cement product were blended, sampled, analyzed for Cu, Ag, Pb, and then used for the chemical upgrading tests.

The chemical upgrading was done by leaching the dried cement product in either hydrochloric acid (4-8 M HCl) or in $FeCl_3$ - 0.3 M HCl solutions with substoichiometric quantities of $FeCl_3$ relative to the lead contained in the cement product. The $FeCl_3$ - 0.3 M HCl solutions contained 3 M NaCl to promote the solubility of lead chloride. In most tests, 2.0 g of cement product was leached in 500 mL of solution for 30 min at 80°C with agitation on a hot plate-stirrer. At the end of the leaching test, the slurry was filtered hot, and a solution sample was taken for AA analysis. The residue was washed with distilled water and then with acetone. The residue was air-dried overnight on the filter paper and was then collected. A small sample of the dried leached residue (~0.1 g) was dissolved in aqua regia and analyzed by AA to determine the solids composition. The product weights could not be determined accurately because part of the metal tenaciously adhered to the filter paper; accordingly, the percentages of the various metals leached were determined from the volume and composition of the solution samples.

RESULTS AND DISCUSSION

Table 1 summarizes the results obtained in the various cementation tests. The cementation rates are very rapid at 85°C with low silver and copper concentrations being realized for retention times of 5 to 30 min. The addition of ∿1.5X stoichiometric lead (tests AgCu -14, -16, -17, -20 and -21) resulted in final solutions containing, on the average, 1.0 mg/L Ag and 30 mg/L Cu. Increasing the retention time from 15 to 20 to 30 minutes did not decrease the final copper concentration of the solution, suggesting that steady state conditions are achieved in <15 min. For >2X stoichiometric addition, steady state conditions seem to be achieved in less than 5 min. The addition of >2X stoichiometric lead to the solution resulted in a final solution containing <1 mg/L each of Cu and Ag even after a 5 min retention time.

The cement product from the test with 2.1X stoichiometric lead addition (AgCu-13) yielded <1 mg/L Cu or Ag, and assayed over 50% Pb. This composition was confirmed in the tests intended to generate cement product for the chemical upgrading tests. When a lower stoichiometric ratio of lead was employed, the product contained significantly less lead. For example, when 1.5X stoichiometric lead was used (AgCu-21), the cement product contained 22% Pb, 68% Cu, 0.9% Ag with 9% unaccounted for and presumably present as chloride or oxide. Reducing the lead dust addition from 2.0X to 1.5X stoichiometric, however, caused the final dissolved copper concentration to increase from 0 to 30 mg/L. Since the primary objective of the cementation step is to reduce the amount of Ag and Cu in the leach solution to <1 mg/L each, the preferred conditions for the cementation step involve the addition of >2X stoichiometric lead dust despite the adverse effects which such large additions have on the composition of the cement product.

Various methods of adding the lead dust were also examined. In test AgCu-20, a total of 1.5X stoichiometric lead dust was used, but the dust was added in three equal increments over the 15 min total retention period. Comparison with test AgCu-21 where the same amount of lead was added in one lot indicates that incremental addition of the lead offers no advantages as concerns either the Cu and Ag concentrations of the final solution or the lead content of the cement product.

The effect of a two-stage cementation reaction on the residue composition and on the final Ag and Cu concentrations of the solution was also investigated. The three parts of test AgCu-22 illustrate the effect of a two-stage cementation process, and the details of this test are summarized in Figure 2. In test AgCu-22(a) only 1.1X stoichiometric Pb dust was added. After 15 min retention time, the residue analyzed 82% Cu, 13% Pb, 1.0% Ag with 4% unaccounted. The solution from test AgCu-22(a), which contained 1.4 mg/L Ag and 290 mg/L Cu, was treated with fresh Pb dust (7.8X stoichiometric) for 10 min in test AgCu-22(b). Solution analysis gave final Ag and Cu concentrations of 1.0 mg/L and 15 mg/L, respectively. The residue from test AgCu-22(b) was added to a fresh solution in test AgCu-22(c). The Pb content of the residue was assumed to be $\sim$1.5X stoichiometric for Ag and Cu removal. After 15 min retention time, the residue analysed 72% Cu, 19% Pb and 0.9% Ag with about 8% unaccounted. The final Ag and Cu concentrations in solution were 1.0 and 201 mg/L, respectively. Thus, a two-stage cementation reaction does not yield very low Ag and Cu concentrations in the final solution (15 mg/L Cu), but does produce a low-lead (19% Pb) and high-copper (72% Cu) final cement residue.

Two batches of cement product were prepared for the chemical upgrading experiments. The first batch weighed 28 g and contained 52.7% Pb, 45.8% Cu

0.89% Ag; the second batch weighed 15 g and assayed 48.1% Pb, 52.7% Cu and 0.92% Ag.

Table 2 summarizes the upgrading tests done using 4-8 M HCl. In every test, significant amounts of lead (determined by analysis of the leach solution) have dissolved to leave a residue containing <10% Pb. When the lead extractions were calculated from the composition of the upgraded residue and the assumption that all the silver reported in this residue, then the percent lead leached increased systematically from 90% in 4 M HCl to 97% in 8 M HCl. Lead chloride is only sparingly soluble in dilute aqueous solutions, and solubility limitations may have biased the results for this element that are presented in Table 2. Approximately half the mass of the sample is dissolved during chemical upgrading although the amounts are difficult to assess accurately as the metals adhere tenaciously to the filter paper. Modest co-extractions of Cu and Ag are also indicated, with <1% Ag dissolution being observed in all instances. If it is assumed that all the input silver reports in the upgraded residue, then the residue compositions suggest higher copper extractions; viz., 12% Cu extraction in 4 M HCl and 49% Cu extraction in 8 M HCl. Further work would be needed to resolve the discrepancies between the two methods of calculating the percentages of the metals leached. The upgraded product is consistently low in lead but contains 69-86% Cu and 1.6-2.6% Ag. That the totals do not sum to 100% is likely attributable to the presence of chloride and/or oxide. The upgraded products produced by any of the hydrochloric acid leaching tests would likely be acceptable to most copper smelters although residual chloride contents may cause problems.

Table 3 presents the results of the chemical upgrading tests done using $FeCl_3$ - 0.3 M HCl media; for these tests the stoichiometric amount of $FeCl_3$

was based on only the amount of lead present in the cement products, according to:

$$2FeCl_3 + Pb \longrightarrow PbCl_2 + 2FeCl_2 \qquad (3)$$

Ferric chloride - hydrochloric acid solutions rapidly attack the cement product, with the total extent of reaction being greater than the stoichiometric amount of $FeCl_3$ would suggest. This is likely due to partial regeneration of the ferric ion lixiviant by air in the leaching vessel:

$$2Fe^{2+} + \tfrac{1}{2}O_2 + 2H^+ \longrightarrow 2Fe^{3+} + H_2O \qquad (4)$$

$$2Fe^{3+} + Cu \longrightarrow Cu^{2+} + 2Fe^{2+} \qquad (5)$$

Large quantities of lead (>80%) are dissolved for all stoichiometric ratios of $FeCl_3$ employed. As was the case for upgrading with concentrated HCl media, higher lead extractions (93-98%) are calculated from the residue analyses and the assumption that all the silver reports in the upgraded residue. Significant amounts of copper are also leached with the extent of leaching increasing from 21% for 60% stoichiometric $FeCl_3$ to 62% for 100% stoichiometric $FeCl_3$. Somewhat higher copper extractions are realized based on the residue composition; for example, for 100% stoichiometric $FeCl_3$, 69% Cu dissolution was calculated. Silver extractions remain relatively constant in the range 0.5 to 1.7%. Although all the products upgraded by ferric chloride leaching have compositions likely acceptable to a copper smelter (<10% Pb, ~80% Cu, 2-7% Ag), the yield of product is somewhat reduced by virtue of the extensive co-dissolution of copper. The test done using 60% stoichiometric $FeCl_3$ resulted in only 21% copper co-dissolution, and this extraction might be acceptable to the process (Fig. 1) as the leach solution would almost certainly be recycled.

Although the $FeCl_3$ - 0.3 M HCl leaching process could probably be made to work, very close control of the $FeCl_3$ stoichiometric ratio would certainly be necessary. Simple upgrading with concentrated HCl solutions would likely be the preferred approach.

CONCLUSIONS

A single-stage cementation reaction employing a 2X stoichiometric quantity of lead dust is able to reduce Cu and Ag to less than 1 mg/L each within 5 min at 85°C. The cement product from this reaction contains ∿50% Pb. Decreasing the amount of lead dust to 1.5X stoichiometric results in a cement product containing ∿30% Pb, but the final solution analyzes ∿30 mg/L Cu, and this copper concentration cannot be reduced by prolonging the retention time. Further decreases in the stoichiometric amount of lead yield lower lead contents in the cement product but result in higher (∿300 mg/L) copper concentrations in the final solution. Incremental addition of the lead dust yields results similar to a one-step addition. A two-stage cementation reaction with 1.1 stoichiometric lead in the first stage and 1.5X in the second stage results in a cement product containing ∿70% Cu and 20% Pb, but the final solution still contains 15 mg/L Cu.

Chemical upgrading of the cement product with either concentrated hydrochloric acid or sub-stoichiometric amounts of ferric chloride seems capable of yielding a product suitable for copper smelting. Solutions containing 4-8 M HCl dissolved most of the lead from the cement product in 30 min at 80°C. In all cases, the upgraded cement product contained <10% Pb together with 70-85% Cu and 1.6-2.6% Ag. Leaching with sub-stoichiometric amounts of $FeCl_3$ - 0.3 M HCl also resulted in the dissolution of lead from the cement product, but appreciable amounts of copper were

also co-leached under all conditions. The extent of copper dissolution increased from ∿20% for 60% stoichiometric $FeCl_3$ to ∿60% for 100% stoichiometric $FeCl_3$; silver extractions, however, were consistently <2%. Although the upgraded products formed by ferric chloride leaching contained <10% Pb, 77-87% Cu and 2-7% Ag, the mass of residue was comparatively low, and this would result in an extensive recycle of dissolved copper within the circuit.

Although the experiments carried out in this program were of a very preliminary nature, they suggest that both copper and silver can be reduced to <1 mg/L by single stage cementation at 85°C using an excess of fine lead dust. Under the preferred conditions, the well-washed cement product would contain ∿50% Pb, ∿40% Cu and ∿1% Ag. Furthermore, chemical upgrading of the cement product is possible, likely using 4 M HCl solutions at 80°C, to give a final product containing <10% Pb, 70-85% Cu and 1.6-2.6% Ag. Relatively minor amounts of Cu and Ag are dissolved in 4 M HCl media. Although the preliminary test work described above has identified the general conditions for recovering Ag and Cu from a hydrometallurgical lead circuit, additional work would be needed on a larger scale with continuous flows and with lead processing solutions to define the optimum conditions for the commercial recovery of these values. In particular, it would be necessary to ascertain the maximum levels of dissolved Cu and Ag which could be tolerated in the processing circuit without leading either to their loss on recycle or to their contamination of the electrowon lead. A further consideration would be to determine the maximum chloride content of the upgraded cement product that would be acceptable to most copper smelters.

ACKNOWLEDGEMENTS

K.G. Tan reviewed the manuscript and provided valuable suggestions concerning both the cementation-upgrading process and the interpretation of the data.

REFERENCES

1 - Dutrizac, J.E. "Recent advances in the leaching of sulphides and in the precipitation of iron"; Proc MINTEK 50; Johannesburg, South Africa; March 1984.

2 - Dutrizac, J.E. "The dissolution of galena in ferric chloride media"; Division Report MRP/MSL 84-14 (TR); CANMET, Energy, Mines and Resources Canada; Ottawa; 1984.

3 - MacKinnon, D.J. and Brannen, J.M. "Silver cementation on copper, lead and zinc from chloride solutions"; Division Report MRP/MSL 82-117 (TR); CANMET, Energy, Mines and Resources Canada; Ottawa; 1982.

Table 1. Summary of Results for the Cementation Tests

Test	Pb Dust Added (X-Stoichiometry)	Dissolved Ag (mg/L)		Dissolved Cu (mg/L)		Retention Time (min)	Residue Composition		
		Initial	Final	Initial	Final		%Ag	%Cu	%Pb
AgCu-3	3.1	25.2	0.8	1455	0	5	-	25	53
AgCu-5	2.0	24.6	0.3	1530	0	5	-	33	40
AgCu-13	2.1	32.4	0.7	1713	0	15	0.8	38	54
AgCu-14	1.6	29.5	1.2	1397	40	15	1.0	66	32
AgCu-16	1.3	32.4	1.1	1673	45	30	1.3	76	19
AgCu-17	1.4	32.8	0.8	1577	92	20	0.8	67	25
AgCu-20*	1.5	30.6	0.8	1557	29	15	0.6	66	25
AgCu-21	1.5	32.9	1.2	1472	24	15	0.9	68	22
AgCu-22(a)**	1.1	31.9	1.4	1604	290	15	1.0	82	13
AgCu-22(b)**	7.8	1.4	1.0	290	15	10	-	-	-
AgCu-22(c)**	1.5	28.3	1.0	1525	201	15	0.9	72	19

CONDITIONS: 1 L solution containing 50 g/L Fe^{2+}, 40 g/L Zn^{2+}, 3.0 M NaCl
0.3 M HCl; 85°C; rapid stirring

* Pb dust added in 3 equal increments at 5 min intervals

** 2-stage reaction

Table 2. Chemical Upgrading Tests Using Hydrochloric Acid

HCl Conc. (M)	Wt. Cement Product Leached (g)	Wt. After Leaching (g)	Percent Leached**			Composition of Upgraded Residue		
			Pb	Cu	Ag	%Pb	%Cu	%Ag
4*	6.00	3.01	81.5	0.4	0.1	9.0	83.1	1.8
4	2.00	-	106.6	0.7	0.1	8.3	72.7	1.6
6	2.00	-	106.3	12.8	0.2	4.1	86.1	2.0
8	2.00	-	64.4	19.5	0.4	4.0	68.9	2.6

* second batch of cement product

** based on solution analyses only

Table 3. Chemical Upgrading Tests Using Ferric Chloride Solutions

Stoichiometric $FeCl_3$ (%)	Wt. Cement Product Leached (g)	Wt. After Leaching (g)	Percent Leached**			Composition of Upgraded Residue		
			Pb	Cu	Ag	%Pb	%Cu	%Ag
60*	6.00	2.43	83.2	20.7	0.5	7.9	84.3	2.2
70	2.00	-	83.7	39.9	1.7	5.9	77.4	3.4
78	2.00	-	88.0	43.0	0.8	5.2	78.2	4.2
85	2.00	-	84.1	51.1	1.1	8.9	79.8	7.4
100	10.73	1.25	91.4	61.7	1.1	7.0	87.6	5.4

* Second batch of cement product

** based on solution analyses only

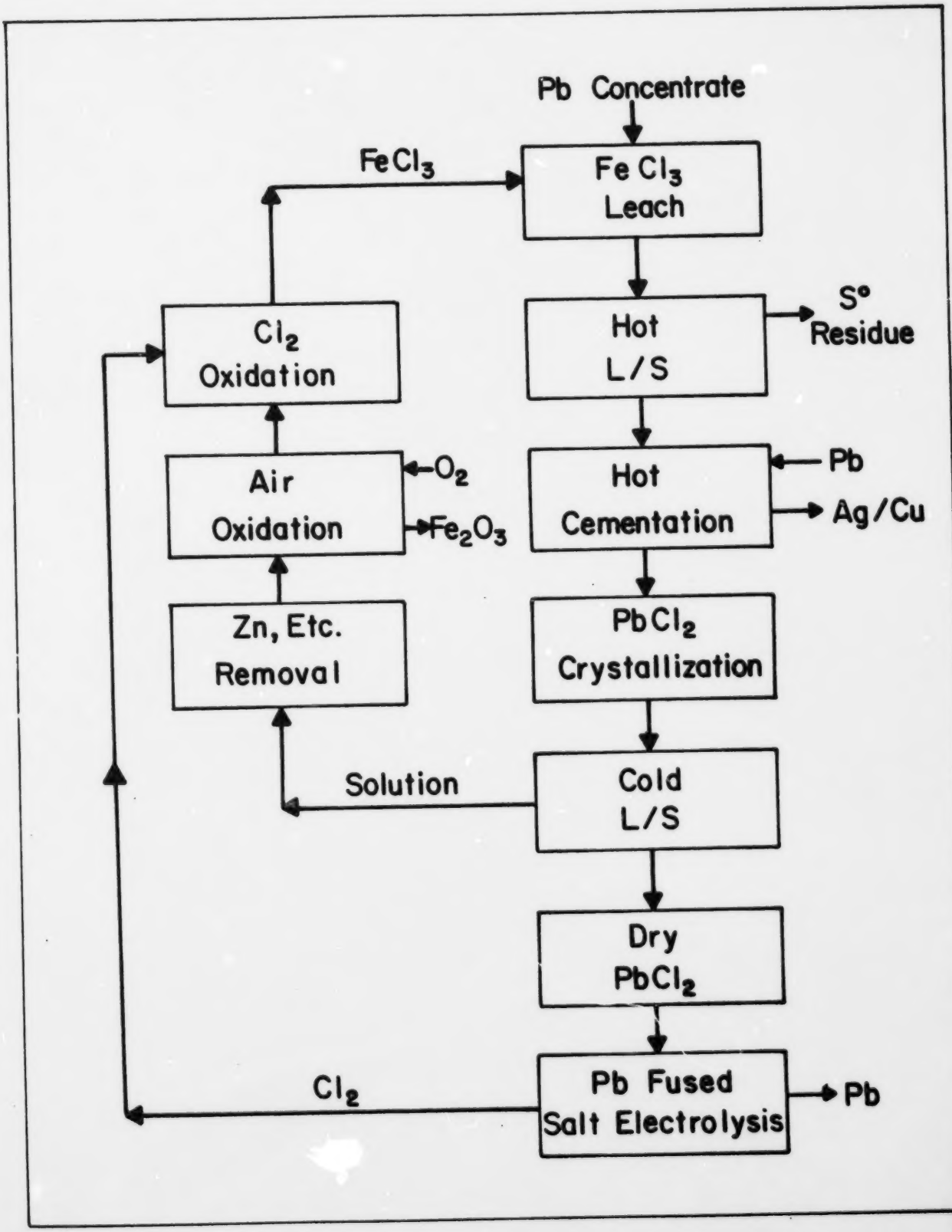

Fig. 1. Schematic Representation of CANMET's Hydrometallurgical Lead Process.

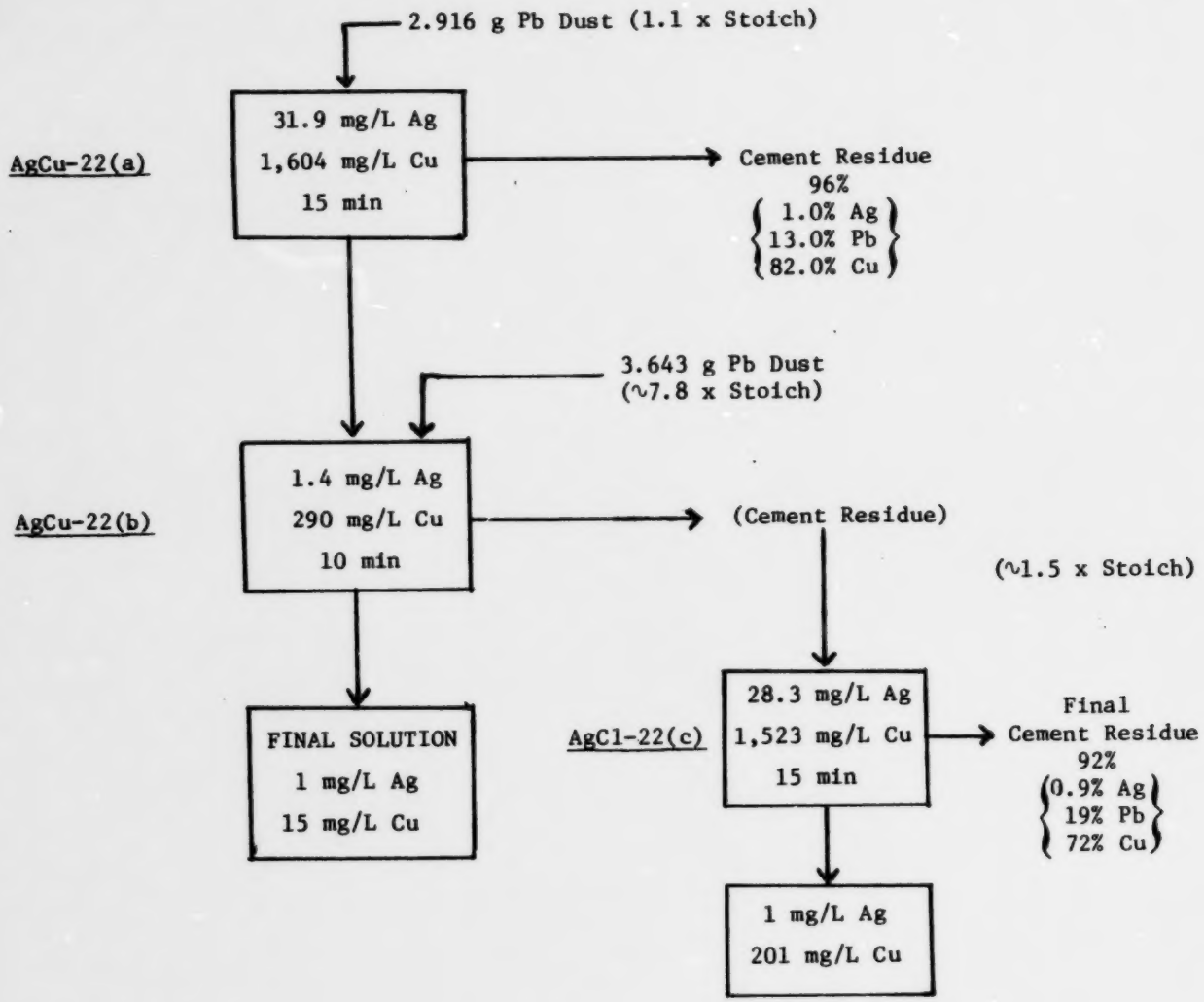

Fig. 2. Schematic Representation of a Two-Stage Cementation Process, Test AgCu-22